Supplementary Information for

Comparison of Acidic Site Quantification Methods for a Series of Nanoscopic Aluminum Hydroxide Fluorides

Felix Hemmann^{a,b}, Christian Jaeger^b, Erhard Kemnitz^{a*}

^a Humboldt-Universität zu Berlin, Department of Chemistry, Brook – Taylor – Str. 2, D – 12489 Berlin, Germany

^b BAM Federal Institute for Materials Research and Testing, Division 1, Richard Willstaetter Str. 11, D-12489 Berlin, Germany

felix.hemmann@bam.de; erhard.kemnitz@chemie.hu-berlin.de; christian.jaeger@bam.de

Calculation of the TOF:

TOFs were calculated by measuring conversion of citronellal after different reaction times. The second stable reaction phase was linear fitted which results in percentage of converted citronellal per hour. The percentage of converted citronellal per hour was further multiplied with the amount of citronellal at the beginning of the reaction (1.6 mmol) and divided by the mass of catalyst (20 mg). This results in TOF of citronellal per mass of catalyst and time $[\mu mol g^{-1} h^{-1}]$.

TOFs were further normalized by the concentration of Brønsted sites (TOF^{BS}) measured by ¹⁵N NMR and by the concentration of all acidic sites determined by three methods NH₃-TPD, PCP and ¹⁵N NMR (TOF^{TPD}, TOF^{PCP} and TOF^{NMR}). The normalized TOFs are converted citronellal molecules per acidic site and per hour [µmol µmol⁻¹ h⁻¹].

SI Table 1. TOFs normalized by the concentrations of Brønsted sites determined by 15 N NMR (TOF^{BS}) and normalized by the concentration of all acidic sites determined by NH₃-TPD, PCP and 15 N NMR (TOF^{TPD}, TOF^{PCP} and TOF^{NMR}).

	TOF	TOF ^{BS}	TOFTPD	TOFPCP	TOF ^{NMR}
	[µmol g ⁻¹ h ⁻¹]	[µmol µmol ⁻¹ h ⁻¹]	[μmol μmol ⁻¹	[μmol μmol ⁻¹	[μmol μmol ⁻¹
		-	h ⁻¹]	h ⁻¹]	h-1]
AlF45	1500 ± 100	60 ± 10	6 ± 1	20 ± 20	16 ± 6
AlF57	3800 ± 600	13 ± 4	9 ± 2	10 ± 10	6 ± 2
AlF75	9600 ± 800	20 ± 4	15 ± 3	13 ± 7	10 ± 3
AlF87	6700 ± 800	15 ± 4	5 ± 1	7 ± 3	6 ± 2

Quantification of acidic sites by PCP:

For the quantification of acidic sites by PCP the curves of conversion of citronellal and selectivity to isopulegol were fitted using two lines for each catalyst. The intersection of these lines was calculated for the conversion and selectivity each. Total concentration of acidic sites, which are accessible to pyridine, in each catalyst is the average of the intersections of these fits. The errors were calculated by propagation of error of the linear fits.



SI Figure 1: Conversion of citronellal and selectivity to isopulegols versus the added amount of pyridine for

the four aluminum hydroxide fluoride samples.

Quantification of acidic sites by ¹⁵N NMR spectroscopy:

To calculate the concentration of acidic sites by ¹⁵N NMR, T₁ values of each resonance have to be known. Torchia spectra with different waiting delays were simulated with two lines in the region of the Lewis signals to obtain chemical shifts and T₁ values of both Lewis signals. This was done for each sample. Simulations showed that one signal with a small T₁ value (about 6 s) is located at about -118 ppm and the second signal with a large T₁ value (about 70 s) at -125 ppm. T₁ values of the signals of pyridine at Brønsted sites and ammonium chloride were also determined; their T₁ values are in order of 6 s. With the obtained chemical shifts the EASY spectra were simulated to compare the signal intensities of the signal at -125 ppm has to be corrected according to the T₁ value. This was done according to equation 1 with A_{site}(70s) the signal intensity determined from the EASY spectra and A_{site} the corrected signal intensity according to T₁.

$$A_{site} = \frac{A_{site}(70s)}{1 - e^{-70/T_1}}$$
(1)

Concentration of acid sites, as number of acid sites N_{site} per sample weight m_{sample} , can be calculated according to equation 2, for this the signal intensities, which were corrected according to their T_1 values, have to be used.

$$\frac{N_{site}}{m_{sample}} = \frac{A_{site}}{A_{NH_4Cl}} \cdot \frac{H_{NH_4Cl}}{H_{pyridine}} \cdot \frac{m_{NH_4Cl}}{M_{NH_4Cl}}$$
(2)

A is the signal intensity, H the abundance of ¹⁵N (98% for pyridine and 7% for NH₄Cl) and m_{NH_4Cl} the mass of the added ammonium chloride as well as its molar mass M_{NH_4Cl} (53.49 g/mol).

Errors of the concentrations of acidic sites were determined in two ways. Firstly, spectra were simulated and concentrations of acidic sites calculated after phase and baseline of the spectra were corrected several times. Furthermore, determination of signal positions contains a certain error, especially for the positions of the two Lewis sites. Therefore, the ¹⁵N NMR spectra were simulated and concentrations of acidic sites were calculated after the positions of the LS II signal was altered by about 1 ppm to lower or higher field.



Additional Figures and Tables:

SI Figure 2: Stepwise adsorption of pyridine (left) and integrated intensity of v_{19b} band of pyridine for pyridine coordinated at Lewis sites and protonated pyridine molecules at Brønsted sites versus pyridine introduced into the FTIR cell (right) for the sample AlF87.



SI Figure 3: FTIR spectra before and after pyridine adsorption at sample AIF57.



SI Figure 4: TPD-IR spectra obtained from the aluminum hydroxide fluoride samples after adsorption of NH₃.

SI Table 2: Conversion of citronellal and selectivity to isopulegol for aluminum hydroxide fluoride samples calcinated at 573 K for two hours.

Sample	Conversion of citronellal [%]	Selectivity to isopulegol [%]	
AlF45	10	54	
AlF57	7	47	
AlF75	10	52	

AlF87	15	57